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OVERTURNING AND ANCHORING OF MONOLAYERS*

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IN some studies of the mechanism of the flotation process made several years ago[1] monolayers of oleic acid were spread on water, and by a dipping process were deposited upon solid surfaces of glass, platinum, mica, calcite, sphalerite and galena. With each of these solids no monolayer was deposited on the down-trip into the water, but on the up-trip the surface came out of the water initially wet and on top of the water film there was a monolayer of oleic acid. After the draining out or evaporation of the water film the hydrophilic groups in the oriented oleic acid molecules were brought into contact with the solid surface to which they adhered more or less firmly, depending on the nature of the solid. Repeated dipping into a clean water surface, dusted lightly with talc, proved that for all the surfaces except mica little or none of the oleic acid monolayer escaped onto the water.

* Address of the vice-president and chairman of the Section of Chemistry, American Association for the Advancement of Science, Indianapolis, December 28, 1937.

[1] I. Langmuir, *Trans. Faraday Soc.*, 15: 62, 1920, reprinted in *G-E Rev.*, 24: 1025, 1921.

Two methods were used for detecting and studying the properties of these deposited monolayers: observations of the lubricating properties and of the contact angles given by drops of water placed on the surface.

The monolayers on the solid surfaces had an enormous effect upon the static friction of small glass sliders placed on the surface. On glass without the film the sliding angle was over 60°, but this was reduced to about 6° by the monolayer.

Drops of water placed upon a clean surface of any of these solids spread over the surface, wetting it completely, thus giving a zero contact angle, θ. The clean surfaces are therefore hydrophilic. After the oleic acid monolayers had been deposited, the surfaces became hydrophobic and the contact angles depended greatly upon the character of the underlying solid. With mica the angle was 18°, 45° for glass, 65° for platinum, 70° for calcite, 82° for sphalerite and 86° for galena.

Mica behaved differently from the other substances

in that a considerable part of the oleic acid monolayer deposited on mica was given up when the mica was dipped into clean water, as shown by the talc test. If the mica covered by the monolayer was repeatedly passed through a stream of water it became wetted nearly as easily as a surface of freshly split mica. The hydrophobic character of oleic acid monolayers on the surfaces of the other substances, however, was not appreciably changed by passages through a stream of water.

According to a theory which I had previously developed[2,3,4,5] the surface tension and presumably the contact angles characteristic of a surface involve only short-range forces and depend primarily on the nature of and arrangements of the atoms which form the actual surface and not directly upon the nature of underlying molecular layers. From this viewpoint because of the orientation of the molecules we might be led to suppose that the upper surface of oil films on solid bodies should always consist of CH_2 or CH_3 groups, so that the surface properties of all the films would be similar.

There is, however, an important distinction between the case of an oil film covered by a water drop and a surface layer of a pure organic liquid. The water drop on the film tends to draw the active groups to itself and so cause a reorientation of the molecules. In the case of oleic acid there are two active groups in the molecule; the carboxyl group and the double bond. We may assume that on galena, with its strong field of force the active groups are held so firmly that water can not cause any appreciable fraction of them to change their orientation. Thus the surface of the oleic acid film on galena consists almost entirely of hydrocarbon groups and the contact angle with water is only slightly less than that observed on solid paraffin ($\theta = 110°$). With a monolayer on glass, on the other hand, the presence of an overlying drop of water may bring some of the active groups to the upper surface of the film, so that the water spreads over this surface much more easily than over paraffin, giving a much lower contact angle.

This theory also readily explains the marked difference between the contact angles of an advancing and a receding water surface on glass covered by an oleic acid monolayer. The advancing surface is continually moving onto a surface having few hydrophilic groups, while at the receding edge of the drop the water must peel back from the surface on which there are many hydrophilic groups produced by the reorientation of some of the polar molecules.

2 I. Langmuir, *Met. Chem. Eng.*, 15: 468, 1916.
3 I. Langmuir, *J. Am. Chem. Soc.*, 39: 1848, 1917.
4 I. Langmuir, *Colloid Chem.*, 1: 525, 1926, edited by Jerome Alexander.
5 I. Langmuir, *Chem. Rev.*, 6: 451, 1929.

Another factor which may cause contact angles to depend upon the nature of the solid under the monolayer is that the spacing of the molecules in monolayers on solids may often be dependent primarily on the surface lattice of the solid, whereas with films on liquids the molecules are able to arrange themselves largely without reference to the structure of the underlying liquid. As a result, the films on solids are ordinarily not in stable equilibrium; many molecules are crowded into spaces too small for them, while others occupy unnecessarily large areas. Even in our early experimental work with films on solids we found that the results were much more irregular and depended much more on slight differences in the previous histories of the films than in the case of monolayers on liquids.

The clean surfaces of glass and the fresh cleavage surfaces of the minerals used in these studies were both hydrophilic and oleophilic, being completely wetted by water or by Petrolatum. However, if very pure Petrolatum was applied first it was found that this was completely displaced from the surface by a drop of water. This displacement could be prevented by very minute traces of fatty acids dissolved in the Petrolatum, for then a hydrophobic adsorbed monolayer was formed between the solid and the hydrocarbon and this could not be removed even by washing with benzene.

Dr. K. B. Blodgett in 1933[6,7,8,9] developed a method of building successive layers of stearates of divalent elements or even of pure stearic acid. Films produced in this way are remarkable in that they are both hydrophobic and oleophobic.

According to Bartell[10] the contact angle θ_R made by a drop of any organic liquid R on a solid can be calculated by the equation

$$\gamma_R \cos \theta_R = (12.8 - \gamma_{RW})K + 65.2 \qquad (1)$$

where γ_R is the surface tension (dynes cm^{-1}) of the liquid (against air), γ_{RW} the interfacial surface tension between the liquid and water and K is a parameter (K_{n3} in Bartell's nomenclature) which is characteristic of the solid only. The contact angle θ_W for a drop of water can be calculated by the same equation if we place $\gamma_{RW} = 0$ and replace the subscript R by W.

Let us consider the application of this theory to drops of water and of Petrolatum (Squibb's) on barium stearate films. Previous measurements[11] have given $\gamma_R = 31.7$; $\gamma_{RW} = 53.0$ and $\gamma_W = 72.8$. Eq. (1) then gives

6 K. B. Blodgett, *J. Am. Chem. Soc.*, 56: 495, 1934.
7 K. B. Blodgett, *J. Am. Chem. Soc.*, 57: 1007, 1935.
8 K. B. Blodgett and I. Langmuir, *Phys. Rev.*, 51: 964, 1937.
9 K. B. Blodgett, *J. Phys. Chem.*, 41: 975, 1937.
10 F. E. Bartell and L. S. Bartell, *J. Am. Chem. Soc.*, 56: 2205, 1934.
11 I. Langmuir, *J. Chem. Phys.*, 1: 756, 1933, see p. 762.

$$\cos \theta_R = 2.10 - 1.29\,K \qquad (2)$$

$$\cos \theta_W = 0.90 + 0.18\,K \qquad (3)$$

According to these equations, hydrophobic solids ($\theta_W > 0$) are those for which $K < +0.56$ while solids are non-wettable by Petrolatum or oleophobic ($\theta_R > 0$) only if $K > +0.85$. Solids whose values of K lie between 0.56 and 0.85 are oleophilic and hydrophilic. This theory, however, denies the existence of any solids which are both oleophobic and hydrophobic.

Now there are numerous surfaces (clean glass, metals, etc.) which are in fact both hydrophilic and oleophilic and these fit in with Bartell's theory. However, the barium stearate multilayers are hydrophobic and oleophobic, as experiments give for water $\theta_W = 90°$ and for Petrolatum $\theta_R = 55°$. If we substitute these values into Eqs. (2) and (3) we obtain $K_R = +1.19$ and $K_W = -5.0$, whereas by Bartell's theory K_R and K_W should be equal.

Bartell's theory was based on observations of contact angles given by 5 liquids on 16 solids. The values of K ranged only from -0.81 to $+0.91$. The discrepancy shown by the stearate multilayers is therefore a very great one, and proves that Bartell's theory can not be generally applicable.

Y-Films: When barium stearate films are built up from stearic acid spread on a solution containing 10^{-4} M $BaCl_2$ 2×10^{-4} $KHCO_3$ at pH 6.8, monolayers are deposited both when the film is lowered into the bath and when it is raised out of the bath. Films of this type we call Y-films. The layers deposited on the down-trip we call A-layers and those formed during the up-trip we call B-layers. Thus Y-films consist of alternating ABAB . . . layers. On the water surface the stearic acid monolayer or H-layer[12] is undoubtedly oriented with the carboxyl group down, and therefore presumably the A-layer has the carboxyl group on the side away from the plate while the B-layer is oppositely oriented so that the tail or hydrocarbon end of the molecule forms the actual surface. Thus in the multilayers the barium atoms should be located in layers with spacings twice the length of the stearate molecule. X-ray examination of the films proves in fact that the spacings of the planes containing the barium atoms is 48.8 Å, while optical measurements prove that the thickness per stearate layer is 24.4 Å.

When water drops are placed upon a barium stearate Y-multilayer, built from H-layers on a solution containing 10^{-4}M $BaCl_2$, 2×10^{-4}M $KHCO_3$ (pH 6.8), the contact angle is 90°. If a drop of water weighing 60 mg is placed on such a prepared plate and this is tilted 25°, the drop begins to move. By decreasing the angle the motion is made to stop, and then the angle at the receding edge is 82° and at the advancing edge 110°. If a drop of Squibb's Petrolatum is used in a similar way the initial angle is 53°, the receding angle 29° and the advancing angle 55°.

The observed hydrophobic character of the Y-multilayers, whose outermost layer is a B-layer, lends support to the view that the molecules are oriented so that the hydrocarbon tail is uppermost. It would seem that direct evidence of the orientation of the A-layer could be obtained by depositing an A-layer on a down-trip and then sweeping off the remaining H-layer by moving a barrier across the water surface so as to avoid the deposition of a B-layer on the up-trip. When this is done, however, it is found that the B-layer escapes onto the water surface. This can be proved not only by observing the motion of talc dusted on the water but also by the direct optical determination of the thickness of the film on the plate by the methods that have been developed within the last few years.[8,9,13,14]

The fact that the film goes back onto the water surface indicates that the force between the water and the A-film is greater than that between the A-film and the underlying B-film, and thus gives support to the belief that the side of the A-film which is furthest from the chromium plate is hydrophilic. We have not yet found any way to anchor the hydrophobic side of the A-layer so as to be able to bring out into the air a hydrophilic A-layer of barium stearate.

It seems remarkable that a substance like Petrolatum should peel off from barium stearate Y-layers when it is considered that the orientation of the uppermost B-layer is such that the actual surface consists entirely of hydrocarbon. The probable explanation is that the molecules are so tightly packed into an area of about 20 Å² per molecule that only the CH_3 groups at the ends of the molecules are exposed on the surface. The properties of CH_3 may well be so different from CH_2 that a liquid consisting mostly of CH_2 does not wet a surface consisting entirely of CH_3.

X-Films: If the pH of the bath from which barium stearate monolayers are deposited onto the chromium plate is raised to about 9, it is found under certain conditions that monolayers are deposited only during the down-trip (A-layers). In this case the plate emerges from the water in a dry condition after each up-trip, giving a contact angle of about 90° with the water, whereas when Y-films are formed at pH 6.8 the contact angle at which the water recedes from the plate on the up-trip is about 50°.

Proof that a film goes on during the down-trip and none on the up-trip is furnished by observing the

[12] The need for a terminology and a symbol for a monolayer of an insoluble substance on water is met by calling such a monolayer an H-layer.

[13] I. Langmuir, V. J. Schaefer and D. M. Wrinch, SCIENCE, 85: 76, 1937.

[14] I. Langmuir, V. J. Schaefer and H. Sobotka, *J. Am. Chem. Soc.*, 59: 1751, 1937.

motion of talc particles placed on the H-layer near the plate. Optical determinations of the thickness of the plate show that the increment of thickness is about 26 to 28 Å per round trip, while with Y-layers it is 48.8 Å per round trip.

There is usually some difficulty in starting the building of X-films. Thus, if after a number of layers of Y-type have been built from a solution at pH 6.8, the pH is changed to 9.0, the first 3 to 4 dips continue to give Y-layers. Then, usually near the edges of the plate and especially near the bottom edge, X-films begin to form. After one or two more dips uniform X-films are deposited over most of the area of the plate.

Dr. Blodgett[9] has found that with solutions of certain pH values it is possible to build either X- or Y-films, depending upon the length of time the film is held under water. If after each down-trip the slide is held 10 sec or more under water, no B-layer is deposited on the following up-trip, so that X-films are built. If, however, the plate is immediately raised out of the solution after the down-trip, a B-layer is deposited on the up-trip so that Y-layers are formed. There appears to be a marked difference of composition between the X- and Y-films. The Y-films are easily skeletonizable by dipping for a few seconds in benzene; this dissolves out the free stearic acid, which may be present to the extent of 10 to 40 per cent., depending on the pH, leaving the thickness of the film unchanged but greatly reducing the refractive index, since each stearic acid molecule is replaced by a void. X-films, however, undergo no appreciable change when dipped into benzene, indicating that there is no appreciable amount of free stearic acid, the film presumably consisting wholly of neutral barium stearate.[15] This increase in barium content occurs spontaneously during the time the film is under water.

Dr. Blodgett has found that X-films of lead stearate are formed from H-layers of stearic acid on 10^{-4}M $PbCl_2$, pH 5.6. If 5×10^{-6}M $SnCl_2$ or 10^{-4}M $FeCl_2$ + 5×10^{-3}M KI, pH 5.4, is added good Y-films of lead stearate can be built. When H-layers of arachidic acid of doubtful purity on 10^{-4}M $PbCl_2$, pH 5.6, are deposited on a chromium plate good Y-films result. In all these cases the Y-films are skeletonizable in benzene, whereas the X-films are not.

Since the X-films consist of a series of A-layers, we should expect them to be so oriented as to give a hydrophilic surface. However, measurements of contact angles obtained with water and Petrolatum on X-films give results practically identical with those on Y-films. We must conclude therefore that in some way the hydrophilic groups in the molecule have been drawn below the actual surface. The practical identity of properties suggests in fact that the deposited A-layer has acquired the same orientation as a B-layer. Thus the molecular layer has overturned, presumably while immersed in the solution.

The structure of X-films is not yet definitely known. There are many apparently contradictory features to be reconciled. X-ray determinations of the spacing between layers of barium atoms in X-films have been made by Holley and Bernstein[16] who find the same spacing as in Y-films. This implies an alternating orientation of successive layers. There is nothing, however, in the method of deposition of X-films to suggest a periodicity corresponding to two round trips.[17]

Porter and Wyman[18] have shown that the potential of the surface of a Y-film on chromium with respect to the underlying metal stays practically constant at about + 0.2 volts as the number of layers in the Y-film increases. With X-films, however, the potential increases linearly with the number of layers, about 70 mv per layer. Porter and Wyman consider this as evidence for internal polarization of the film such as would be expected if all the layers had similar orientation, a result in conflict with Holley and Bernstein's measurements.

Porter and Wyman in a second paper[17] show that the total potential of a composite film consisting of X- and Y-layers is brought nearly to zero by the addition of one or two pairs of Y-layers, whereas one or two X-layers raise the potential nearly as high as if the whole film were built of X-layers. These results seem to indicate that the potentials of the X-layers are not due to internal polarization but are caused by a surface electrification or a kind of frictional electricity, generated by the recession of water from the hydrophobic surface during an up-trip. In the case of Y-films there is no such recession from a surface, for the water between the B-layer and the underlying A-layer is forced out by an attraction between the hydrophilic groups of layers by a kind of zipper action.[13] There is thus none of the slipping of one surface over another which would seem to be needed for the development of frictional electricity.

If the potentials of the X-films are due to a surface charge, the potential should increase in proportion to the number of layers. There is then no evidence from the experiments against an alternating arrangement for the layers inside the X-films. The uppermost

[15] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, 58: 284, 1936.

[16] C. Holley and S. Bernstein, *Phys. Rev.*, 52: 525, 1937.

[17] (Private communication from E. F. Porter and J. Wyman, Jr.) In their second paper, *J. Am. Chem. Soc.*, 60: 1083, 1938, Porter and Wyman give evidence that during the early stages of the building of X-films the electric potentials and the contact angles show alternating increases and decreases, indicating a periodicity corresponding to two dips.

[18] E. F. Porter and J. Wyman, Jr., *J. Am. Chem. Soc.*, 59: 2746, 1937.

layer, however, presumably always has an orientation similar to that of a B-layer.

The suggestion has been made by Porter and Wyman[17] that X-films with an odd number of layers have structures like Y-layers, with alternating orientations throughout the film.

When one more A-layer is deposited, making the total number even, this new layer overturns to give an orientation like that of the B-layers of a Y-film, so that now the outer two layers have similar orientation. When a second A-layer is deposited, giving again a film with an even number of layers, it is then necessary that the new layer and the one below it shall both overturn, in order to reestablish the alternating orientation characteristic of the odd number of layers.

A convenient way of representing the structures of built-up films is to employ the small (l.c.) letters p and q. Two layers which have molecules oppositely oriented so that their "heads" face one another are thus shown as pq, while qp represents two layers having the "tails" of the molecules in contact.[19] If we adopt the convention of placing P, which represents the solid plate at the left with the symbols for the successive layers to the right of it, Porter and Wyman's suggested structures of X-films (in air) are: P qp qp q for 5 layers, P(5), P qp qp qq for P(6) and P qp qp qp q for P(7).

An odd-numbered layer, such as the outside layer in P(5), must originally have been deposited as a p-layer (A-layer), but overturned to give a q-layer before being brought out into the air. It remains as a q-layer in P(6) and P(7).

An even-numbered layer, such as the outside layer in P(6), starts out as a p-layer when deposited, overturns to give a q-layer before being brought out into the air, and overturns again, back to a p-layer, in P(7) probably at the time when the outside layer of P(7) overturns.

Thus the q-layer which constitutes the outside layer of an X-film in air overturns to give a p-layer when another layer is placed on it, *unless the heads of the molecules in the q-layer are in contact with* (or anchored by) *the heads of an underlying p-layer.*

The slight alternations observed by Porter and Wyman[17] in potentials and contact angles are probably to be explained as due to a less complete orientation of the outside q-layer (even number of layers) than when the outside q-layer is more firmly anchored by an underlying p-layer (odd number of layers).

Whatever the structure of X-films may ultimately turn out to be, it seems that overturning of layers must be involved in their formation.

Skeleton Films: The comparative stability of skeleton films of lead, cadmium or barium stearate which contain as much as 40 per cent. of voids seems to indicate an extraordinary rigidity for the hydrocarbon chain. To form a void or hole in a solid substance such as a barium stearate layer should require an energy roughly equal to the heat of evaporation of a molecule, which in the case of stearic acid must be very large. Thus the collapse of a skeleton film should involve a large decrease of free energy and should be an irreversible process.

Professor Edward Mack, Jr., has given me some models of hydrocarbon chains in which the carbon atoms are represented by aluminum spheres 1.54 cm in diameter, connected by rod-shaped axes about which the spheres can be rotated freely. The scale of the model is such that 1 cm corresponds to 1 Å. Hemispheres of a diameter of 2.0 cm with their centers in positions corresponding to the hydrogen nuclei determine the distance of nearest approach of hydrogen atoms in neighboring hydrocarbon molecules.[20] When this model of the hydrocarbon chain is placed on a flat surface it is possible to arrange the carbon atoms in a zigzag which corresponds to the crystal structure of stearic acid. The molecule as a whole then has roughly the form of a rectangualr prism, 4.3×3.9 Å with a cross-section which corresponds to 17 Å^2, only a little less than the 19.2 Å found for the cross-section of hydrocarbon chains in crystals of hydrocarbons. As long as the molecule rests on a flat surface it acts as a rigid body. If, however, it is lifted off the flat surface, it can be rolled up nearly into a sphere or into a great variety of other shapes.

In barium stearate films the hydrocarbon chains have their axes perpendicular to the plane of the film and each is probably surrounded by 6 neighboring chains. If half the film consists of stearic acid and this is removed by skeletonization, each molecule of barium stearate remains in contact with about 3 out of the 6 neighboring molecules. The free rotation around the carbon-carbon linkage takes place about an axis inclined 35° from the axis of the hydrocarbon chain. The presence of neighboring molecules can thus prevent free rotation so that the molecules are held in a rigid form and collapse is prevented.

Mechanism of Overturning: The rigidity of the hydrocarbon chains, illustrated by the properties of skeleton films, is in striking contrast to the mobility required for the overturning of molecules or even

[19] To avoid confusion due to overturning it seems necessary to use A and B as symbols to denote only the *method* of *deposition* (down-trip and up-trip) and not the orientation of layers. Thus Y-films are PBABAB . . . AB and X-films are PRAB . . . AA, although the orientation of their layers may perhaps be the same. In Y-films the A- and B-layers correspond respectively to p and q layers but because of the overturning there is no such relationship in the X-films. The orientation of p layers may be described as *exotropic* (having the head turned out) while that of q layers is *endotropic* (head turned in).

[20] Edward Mack, Jr., *J. Am. Chem. Soc.*, 54: 2141, 1932.

whole layers of molecules within solid multilayers. It is inconceivable that rigid molecules could turn end over end in these films. However, the models of Dr. Mack indicate that a hydrocarbon chain if freed from the constraint of its neighbors can bend into a U-form in which the two legs of the U, and the semicircular bend between them, have a total cross-section of only 40 $Å^2$. Thus in the q-layer of barium stearate which constitutes the outside layer of an X-film, a single barium atom joins two adjacent stearic radicals, forming a kind of U. By a kind of ring-around-the-rosy motion the U-shaped molecule is changed into a C-shaped molecule by the gradual shortening of one leg and the lengthening of the other, whose free end bends down to follow the receding short end. In this way, by a continuous process, the whole molecule of barium stearate turns from a U into an inverted U and so the barium changes its position to the opposite side of the monolayer. The overturning of the monolayer thus depends upon free rotation about the carbon-carbon bonds but for each molecule requires a space no greater than that of a prism of cross-section of 20 Å and a length of 25 Å.

Although the stability of skeletonized films shows that the hydrocarbon chains are sometimes extraordinarily rigid, the extreme rapidity with which such skeletons are formed by dipping stearate films in benzene for 1 second proves very high internal mobility. During this short time benzene molecules must penetrate into the film to a depth of 100 or 200 barium stearate layers (5,000 Å) and displace the stearic acid molecules from their positions. Skeletonization is possible (at a rate 100 times slower) even if the Y-film is covered by a "blanket film" of 20 layers of neutral barium stearate which itself is not skeletonizable.[13]

Overturning of B-Layers by Thorium Nitrate. The A-layers deposited on the down-trip during the building of a Y-film are exotropic and therefore, if aluminum chloride or thorium nitrate is introduced into the solution after the down-trip, we should expect the polyvalent cations to combine with the carboxyl groups and so join them together that the A-layer can no longer escape onto the water surface during the up-trip. Thus we should produce a hydrophilic A-layer. These predictions were completely verified by experiments.[21]

Subsequently it was found[22] that a B-layer could be conditioned in this way by solutions of polyvalent cations just as well as an A-layer, the film being made hydrophilic. The B-layer of a Y-film is endotropic, and so there is no obvious reason for expecting interaction of the film with cations in the solution since only the hydrocarbon parts of the molecules are exposed. We must conclude that the B-layer has overturned and been changed from a q- to a p-layer. We may assume that thermal agitation causes individual molecules to overturn from time to time, the number in reversed orientations at any one time being extremely small, although a given molecule may overturn many times per second. If the plate is now dipped into thorium nitrate, the molecules which do overturn spontaneously become anchored by the thorium ions and are so prevented from returning to their original orientation.

Dr. G. H. A. Clowes has reported that barium stearate films can be conditioned by uranyl salts at pH 6 but at pH 5 or 7 this treatment does not render the surface hydrophilic. We have found that the Y-barium stearate films, rendered hydrophilic by the 10^{-3}M uranyl nitrate solution at pH 6, remain so if washed with distilled water in equilibrium with the CO_2 of the air at pH 5.8, but immediately become hydrophobic if washed with distilled water which contains less CO_2, pH 6.6. However, a few drops of water of pH 5.8 again render the surface hydrophilic. Apparently this action can be repeated indefinitely. We have found a few other cases (sodium desoxycholate) where very slight changes of pH may change conditioned surfaces reversibly from a hydrophilic to a hydrophobic condition. Perhaps these are due to overturning of the surface layers. The phenomenon is one which deserves much further study.

Protein Films: Protein H-layers can be deposited on plates covered by barium stearate films either as A-layers or as B-layers. Many proteins, for example zein and gliadin, and others in less degree, give hydrophobic films when deposited at surface pressures $F < 10$ dynes/cm, but at higher pressures the surfaces become hydrophilic. There is no appreciable difference, however, between A- and B-films in this respect. This seems to indicate that the A- or B-films can readily overturn in response to the conditions to which they are exposed. For example, if a drop of water is placed on the surface, the hydrophilic side chains are moved to face the water, whereas when an oil drop is placed on the surface the hydrophobic groups move into contact with the oil.

The reactivities of the protein monolayers also seem to be the same whether the layers are of A or B types. Presumably, however, the reactivities and other properties should depend on orientation. It was therefore desirable so to anchor the hydrophobic or the hydrophilic groups in the protein film that these can not overturn. If a B protein monolayer is deposited on a stearate plate conditioned with thorium nitrate, the hydrophilic groups in the protein become anchored to the thoria. Such a surface is much more highly hydrophobic than a protein film deposited directly onto barium stearate.

[21] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, 59: 1406, 1937.

[22] I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, 59: 1762, 1937.

By conditioning a stearate plate with thorium and then treating with sodium desoxycholate, the surface is rendered extremely hydrophobic. The desoxycholic acid has a great affinity for hydrocarbons, and thus when a B-layer of protein is deposited on a surface conditioned with desoxycholate the hydrophobic parts of the protein are anchored, while the hydrophilic groups are left free to form the actual surface. Protein films prepared in this way were found to be hydrophilic.

The chemical activities of urease monolayers[23] deposited and anchored in these two ways were found to differ markedly in their ability to convert urea into ammonia. The hydrophobic surface of urease adsorbed on the surface conditioned with thoria was very reactive, whereas the hydrophilic urease adsorbed on desoxycholate showed no appreciable activity.

Anchoring of Fatty Acid Monolayers on Glass and Chromium. In depositing the initial B-layer of stearic acid on the clean glass or chromium, preparatory to the building of multilayers, Dr. Blodgett[7] found that the pH of the water and the presence of certain cations were of great importance in determining the adhesion of the monolayer to the plate. In the early work on monolayers of oleic acid on the surfaces of minerals[1] ordinary tap water had been used and no study of the effect of the pH was made. With the assistance of Mr. C. N. Moore I have recently undertaken experiments with monolayers of oleic and stearic acids on glass and chromium plates.

A microscope slide cleaned in a sulphuric-chromic acid mixture, washed thoroughly with distilled water and dried was coated with oleic acid or stearic acid in several ways and was then tested by placing a drop of water on the surface and observing the contact angle. B-layers of oleic or stearic acid, deposited from H-layers on distilled water, were displaced from the glass surface by a drop of water placed on the glass, leaving the glass completely wetted by water ($\theta = 0$). On the other hand, if a portion of a dry glass surface was moistened with 0.1 M sodium hydroxide or barium hydroxide solution, and this was then thoroughly washed with distilled water, the oleic or stearic acid B-layers were hydrophobic and adhered firmly to the glass on those parts of the surface which had been treated with the alkali. In the case of the surface which had been treated with sodium hydroxide the contact angle against water was 20°, while the surface treated with barium hydroxide gave 40°. An essentially similar result was obtained when the cleaned glass plate was washed with Schenectady city water which contains the equivalent of about 40 parts of $MgCO_3$, 72 of $CaCO_3$, and 77 $CaSO_4$ per million.

We also tried applying liquid oleic acid directly to the glass. This film was completely displaced by water unless the glass had previously been treated with alkali. Stearic acid, however, when melted on the clean glass surface forms drops which show a large contact angle against the glass (oleic acid on glass gives a practically zero contact angle). The glass so treated was hydrophobic and gave with water a contact angle of about 20°.

By dipping dry clean glass surfaces into dilute solutions of oleic or stearic acid in benzene, monolayers of the acids were adsorbed from *solution*. The layers formed in this way, which we shall call S-layers, were immediately displaced from the surface by the addition of a few drops of water, giving a hydrophilic surface. Treatment with sodium hydroxide or barium hydroxide before applying the benzene solution gave hydrophobic surfaces.

In each of the foregoing cases which gave a hydrophobic surface the contact angle was not lowered by repeatedly passing the plate through a stream of running water. It was also not markedly altered by repeated dipping into pure benzene or by heating to 100° C.

A series of tests were made with films of oleic and stearic acid applied in various ways to surfaces of chromium plated brass which had been thoroughly cleaned by polishing with shamva. An oleic acid S-layer applied from a benzene solution and a B-layer both gave contact angles of $\theta = 55°$ when a drop of water was placed on the surface. There was a considerable hysteresis, however, for when the slide was tilted the angle at the advancing edge of the drop rose to about 90°, while at the receding edge it fell to 40°. Drops of Petroleum gave advancing angles of 3° and receding angles of 0°, so that the surfaces were oleophilic.

Molten stearic acid on chromium draws up into drops and leaves on the metal a monolayer which shows a contact angle for water $\theta > 90°$ and about 30° for Petrolatum. When clean chromium was treated with a dilute solution of stearic acid in benzene and was then washed in pure benzene, an S-layer was left which gave a contact angle of 70° with water. A drop of Petrolatum gave a contact angle of about 5–10° and a receding angle only slightly greater than zero; that is, the oil drop peeled back from the surface extremely slowly with a hardly perceptible contact angle.

The S-layers of the fatty acids on glass or chromium and the B-layers of oleic acid on glass were oleophilic, whereas barium stearate Y- or X-films are oleophobic, giving $\theta = 53°$.

The difference between the S- and B-layers of stearic acid is probably due to a regular close-packed arrangement of the molecules deposited from an H-layer, while the molecules of stearic acid that diffuse to the surface

[23] Paper by I. Langmuir and V. J. Schaefer to appear in the June number of the *J. Am. Chem. Soc.*

in the benzene solution to form the S-layer are far less regularly spaced. The contact angles θ we have been discussing are measured by placing drops of liquid on the surface of a monolayer on a solid. This angle serves as a measure of the work of adhesion W given by

$$W = \gamma\ (1 + \cos\theta)$$

where γ is the surface tension of the liquid of the drop.

Zipper Angles: There is another angle, which we shall call the *zipper angle, z,* that measures the adhesion of a B-layer for an underlying surface. For example, a clean chromium slide is immersed in clean water and then an H-layer of stearic acid is spread on the water. The water appears to peel back from the slide as this is slowly withdrawn from the water, leaving the slide dry but with a B-layer which has been deposited on its surface. Actually, however, the water is forced out[13] from under the B-layer by attractive forces exerted by the polar groups of the B-layer upon the underlying polar atoms of the chromium surface—a kind of "zipper-like" action. The force of gravity is entirely inadequate as a cause of this phenomenon. The angle z is conveniently measured by withdrawing the slide from the water in an inclined position (its surface inclined from the horizontal by the angle z) and so altering z that the water surface remains horizontal right up to the line of contact with the plate. The angle is readily measured within about 10°.

Oleic or stearic acid B-layers deposited on glass from pure water gives $z = 0$; *i.e.,* the water is not forced out from under the B-layer. Such a B-layer is described as a *hydrous* B-layer, as it is separated from the underlying plate by a relatively thick layer of water (several microns at first). On standing a few minutes in the air the water film evaporates and the B-layer (then called a dehydrous B-layer) then comes into contact with the glass. If the glass has been previously treated with alkali, this B-layer becomes firmly anchored to the glass and can not be displaced by water or dissolved off by benzene.

Recent experiments have shown that B-layers of oleic, stearic and arachidic acids deposited on clean glass from H-layers on distilled water are hydrous, $z = 0$, even if the pH is adjusted to values from 4 to 9 by HCl, $NaHCO_3$ or NH_4OH.

B-layers of these acids deposited on a Shamva-polished chromium surface give zipper angles $z = 50$ to 60°, so that the plates emerge dry. These B-layers are firmly anchored to the chromium plates and are not displaceable by water or soluble in benzene.

CONCLUSION

The structure and surface properties of monolayers and multilayers are frequently determined by the orientations of individual molecular layers, but under certain conditions a layer may undergo an almost instantaneous reversal of orientation. This overturning may alter the chemical and physical properties.

It seems probable that the overturning of molecular layers may be a phenomenon of considerable biological significance. If the monolayers contain dipoles or ionic charges as well as hydrophobic and hydrophilic groups, the overturning of the layer may cause large changes of electric potential. Conversely, change of potential or of chemical composition of the liquid on one side of a membrane may cause an overturning of one or more of the monolayers and so change the properties of the film. The phenomenon of overturning may perhaps help explain the mechanism of the propagation of nerve impulses.

SCIENTIFIC EVENTS

REPORT OF THE TRUSTEES OF THE BANTING RESEARCH FOUNDATION

A TEN-YEAR period has elapsed since the first group of grants was made by the trustees of the foundation. During this period grants have been made annually in accordance with the charter to the Department of Medical Research under Sir Frederick Banting; and also 184 grants have been made to 110 individuals distributed throughout Canada as follows: Brandon College 1; Dalhousie University 10; McGill University 18; Queen's University 2; University of Alberta 3; University of British Columbia 1; University of Manitoba 13; University of Saskatchewan 2; University of Toronto 56; University of Western Ontario 5.

[24] I. Langmuir, *J. Franklin Inst.,* 218: 143, 1934, see p. 156.

During the year 1936–37, 28 workers received grants from the foundation and 24 papers have been published as the result of grants made in this or previous years. The following brief comments may be made on the grants made during the year:

B. F. Crocker, University of Toronto: A new method is being employed for the study of the process of digestion in dogs and satisfactory progress is being made. Dr. J. C. Goodwin, University of Toronto: A further payment was made in order to have a technical analysis of the report made on the observations made in regard to the relationship between the inter-racial origin of parents and the progress of labor. Dr. E. R. Grant, McGill University: On the cause of otosclerosis. Dr. A. W. Ham, University of Toronto: A valuable research was carried out on the changes in joint cartilage produced by vitamin C. Mrs.

H. T. Malloy and K. A. Evelyn, McGill University: On the determination of bile in blood, using the new photoelectric colorimeter. B. Schachter, University of Toronto: Purification of the gonadotropic substance in human pregnancy urine. Drs. D. L. Selby and R. W. I. Urquhart, University of Toronto: on the effect of experimental unilateral nephrosis on the secretion of urine. Dr. S. Weinstein, University of Toronto: An attempt to crystalize prolan. Drs. R. F. Wilkinson and R. G. MacKenzie, University of Toronto: A clinical study of the prevention of thrombosis in man by means of heparin. R. J. Wilson, University of British Columbia: A study of the type of staphylococcus which produces food poisoning in man. Dr. B. Chown, University of Manitoba: On some types of kidney disease which are probably due to an excess of mineral secretion. Dr. D. Beall, University of Toronto: An attempt to introduce an amino group in oestrone and oestrodiol. Dr. G. H. Ettinger, Queen's University: An endeavor to account for the large amount of acetylcholine contained in the placenta. E. J. Reedman, University of Toronto: On free and combined vitamin C.

V. E. HENDERSON
A. W. HAM
Honorary Secretaries

CHANNEL ISLANDS NATIONAL MONUMENT

BY proclamation of President Roosevelt, two of the Channel Islands, off the coast of southern California, have been transferred from the Bureau of Lighthouses of the Department of Commerce to the Department of the Interior, to be established as a national monument by the National Park Service.

Five islands are included in the Channel Islands group, which were discovered in 1542 by the Portuguese navigator, Juan Rodriques Cabrillo, whose remains are buried on San Miguel. The two now given national monument status are Santa Barbara and Anacapa. The latter is in reality three small islands, but these lie so nearly in a straight line, with such narrow channels between them, that they have long been considered as a single island. Combined length of the three is approximately four and a half miles, with a maximum width of about half a mile. High sea cliffs, almost perpendicular, are characteristic of the Anacapa group, with numerous wave-cut caves eroded into their forbidding declivities. The highest elevation is 980 feet. Santa Barbara's length is one and a half miles; its maximum width, one mile. There are so few breaks in its bold, precipitous shores that but one landing place is possible, and that is accessible only in mild weather. Except for two hills, one 547 feet in elevation, the top of the island is a comparatively flat expanse, bordered by steep cliffs.

The monument has been established to conserve the unique geological and biological features of the two islands. Both present fascinating geologic stories; both consist largely of volcanic rocks of the Miocene age. In some places three distinct elevated beaches are clearly defined by terraces along the high cliffs. In these a wealth of fossils has been found, ranging from marine invertebrates to Pleistocene elephants and fossil trees.

More than eight endemic flowering plants, some thirty endemic mammals or birds, and sixteen land mollusks add further to the scientific fascination of the two islands. As research reserves, available for study, the islands will not for the present require any development.

THE ENDOWMENT OF THE BIOLOGICAL SCIENCES AT THE UNIVERSITY OF CHICAGO

THE Rockefeller Foundation has made a conditional grant of $1,500,000 to the University of Chicago for the endowment of research in the biological sciences on condition that an additional sum of $500,000 can be obtained from outside sources before June 30, 1941.

During the next three years the foundation will provide $180,000, at the rate of not more than $60,000 a year, for biological research. This grant has been made so that the equivalent of the income of the capital sum of $1,500,000 will be available to the university during the period allowed for raising the matching sum of $500,000. Should the university be able to meet the condition in a shorter period, the temporary annual grants will be cancelled. Since 1929 the foundation has provided grants for the support of basic laboratory research in fundamental biological problems. The endowment will support permanently this work on a somewhat larger scale than in the past.

Dr. Robert Maynard Hutchins, president of the university, made a statement in which he said:

> Because this grant is one that is vital to the university's research in the cause and treatment of disease, we shall make every effort to secure the matching funds from friends of the university.
>
> Fundamental research in the biological sciences must be carried on to achieve systematic advance in medicine. When the General Education Board gave us $3,000,000 in December, 1936, to develop our Medical School, it specifically recognized this relationship.
>
> The university's clinical work, conducted for research purposes, is in close cooperation with the natural sciences departments. We recently appointed an eminent physicist, Dr. James Franck, to a professorship in physical chemistry to study a biological problem. Medical research at the university to-day is a cooperative enterprise reaching from the hospitals into such remote fields as botany. The offer of the foundation, therefore, is of great importance to our program.

Many of the investigators at the university and much of its important research work have been supported in part by the annual grants of the foundation

during the past ten years. According to Dr. William H. Taliaferro, dean of the Division of Biological Sciences, the grants have "yielded results out of all proportion to the sums invested." The money has been used to provide impetus to long-term projects begun and partly financed with university funds, and to begin new projects of unusual promise.

The recent discovery by Dr. Lester Dragstedt of lipocaic, the hormone which enables diabetics to utilize fat, as insulin does sugar, was one of the projects supported by the annual grant. Two of the most important of the long-term projects assisted were the work of Professor Fred C. Koch, biochemist, on sex hormones, and the studies of Professors Frank R. Lillie and Carl R. Moore on the biology of sex. The research of Dean William H. Taliaferro on the mechanism of immunity, particularly to diseases caused by parasites, also received allotments from the grants.

Allotments were made last year to twenty-six projects, ranging from $100 to $14,000. These included research in bacteriology, anatomy, botany, physiology, biochemistry, neurology, psychology, zoology and mathematical biophysics.

THE ANNUAL MEETING OF THE AMERICAN SOCIETY FOR TESTING MATERIALS

THE forty-first annual meeting of the American Society for Testing Materials will be held at Chalfonte-Haddon Hall, Atlantic City, from June 27 to July 1, inclusive. There will be as many as seventeen technical sessions in order to provide adequate time for the authors and for reports of chairmen of the committees, and also for those who will present written and oral discussion of the papers.

The annual address of the president, Dr. A. E. White, will be given at the opening session on Tuesday morning, June 28. Evening sessions will be held on three days. There will be no technical sessions on Monday, June 27, which will be available for meetings of committees. Additional committee meetings will be held on Thursday afternoon.

The thirteenth Edgar Marburg lecture will be delivered on Wednesday afternoon at 4 o'clock by Dr. Albert Sauveur, professor emeritus of Harvard University, on "The Torsion Test." Following the presentation of the Marburg lecture, the award of the Charles B. Dudley medal will be made to Robert H. Heyer, of the Research Laboratories of the American Rolling Mill Company, for his paper entitled "Analysis of the Brinell Hardness Test" presented at the annual meeting in New York City in 1937. Mr. Heyer's paper was selected by the Dudley Medal Committee as being "an outstanding contribution in the field of research."

The most important session from the technical standpoint will be a symposium on impact testing. This is being developed in cooperation with the Welding Research Committee of the Engineering Foundation. W. W. Werring, of the Bell Telephone Laboratories, Incorporated, chairman of the Section on Impact Testing of Committee E-1 on Methods of Testing, and M. F. Sayre, professor of applied mechanics, Union College, who is representing the Welding Research Committee, are in charge of preparing the symposium.

VERNON LYMAN KELLOGG

THE following resolution has been adopted by the Division of Biology and Agriculture of the National Research Council:

Vernon Lyman Kellogg was born in Emporia, Kansas, on December 1, 1867. He attended the University of Kansas where he graduated in 1899. Here he became assistant professor of entomology in 1890 and private secretary to Chancellor F. H. Snow in which positions he remained until he was called to Leland Stanford University in 1894 as assistant professor. He was closely associated with President David Starr Jordan and collaborated with him in giving courses and in the production of numerous text books. During the World War he worked with Herbert Hoover in relief work in Belgium and France. Upon his return to this country he became active in the formation and administration of the National Research Council in which he was chairman of the Division of Biology and Agriculture. Upon the permanent establishment of the National Research Council he became its secretary, in which office he continued active until ill health forced him to retire in 1932.

He was largely responsible for the administration of the council and held positions upon several of the divisions and innumerable committees. In all this work he was tireless, efficient and influential in securing harmonious action. Under his direction the business of the council proceeded through the formative years without delay or conflict. He was thoughtful and considerate of others and did not spare himself in the service of the organization for which he had relinquished his career as a teacher and investigator. Still devoted to the application of science to human living, however, he wrote extensively upon many topics, always interestingly, authoritatively and well. Although in recent years unable to carry on active work at the council he retained until the last a lively interest in its affairs and personnel. After a long and distressing illness he finally put aside the heavy burden at Hartford, Connecticut, August 8, 1937.

The Division of Biology and Agriculture here records its heartfelt appreciation of his services in the division and in the wider circle of the council as a whole. It desires particularly to record its high estimate of him as a man and a fellow worker in science.

RECENT DEATHS

DR. JOHN J. ABEL, who retired with the title emeritus in 1932 from the professorship of pharmacology

at the Johns Hopkins University, director of the Laboratory of Endocrine Research, died on May 26 at the age of eighty-one years.

DR. ELMER PETER KOHLER, Sheldon Emery professor of organic chemistry at Harvard University, died on May 24 at the age of seventy-two years.

DR. A. E. ALDOUS, professor in the department of agronomy of the Kansas State College of Agriculture and Applied Science, died suddenly on May 5 at the age of fifty-one years.

MERRITT W. HARPER, professor of animal husbandry in the New York State College of Agriculture at Cornell University, died on May 10 at the age of sixty years.

DR. SINCLAIR SMITH, physicist at the Mount Wilson Observatory, died on May 18, at the age of thirty-nine years.

DR. FRED BAKER, the conchologist, died in San Diego on May 16 in his eighty-fourth year. His collection of shells, said to be the largest privately owned collection in the West, will go to the San Diego Society of Natural History, of which he was vice-president.

DR. WILLIAM EAGLE CLARKE, a leading British ornithologist, formerly keeper of the natural history department of the Royal Scottish Museum in Edinburgh, died on May 12 at the age of eighty-five years.

DR. MAX NEISSER, professor of hygiene and bacteriology at Frankfort-on-Main, has died at the age of sixty-nine years.

SCIENTIFIC NOTES AND NEWS

AT a meeting of the Royal Society on May 19 Dr. Niels Nørlund, professor of mathematics at the University of Copenhagen and director of the Danish Geodetic Institute, was elected a foreign member. The election of Professor John Jacob Abel, director of the Laboratory of Endocrine Research at the Johns Hopkins Medical School, was announced last week. Dr. Abel has since died at the age of eighty-one years.

DR. WENDELL MEREDITH STANLEY, of the Rockefeller Institute, Princeton, N. J., in recognition of his achievement in isolating crystalline forms of the filterable viruses, has been awarded the Rosenberger Medal of the University of Chicago, founded by Mr. and Mrs. Jesse L. Rosenberger, "for distinguished achievement in the advancement of learning or for notably great service in the promotion of human welfare."

THE Lamme Medal "for meritorious achievement in engineering" will be presented at the commencement exercises of the Ohio State University to Professor Emeritus James E. Boyd, for twenty-eight years chairman of the department of mechanics.

DR. H. H. RUSBY, emeritus dean of the New York College of Pharmacy, Columbia University, has been awarded the Flückinger gold medal for 1937 by the National German Apothecary Association.

DR. JOHN W. TURRENTINE, president of the American Potash Institute, Washington, D. C., has been awarded the gold medal of the Académie d'Agriculture de France. Dr. Turrentine was an official delegate of the United States at the tenth International Congress of Chemistry recently held in Rome.

DR. CHARLES E. COATES, dean emeritus of the State University of Louisiana, was presented on May 14 with the Herty Medal in recognition of his research work with sugar. The medal is presented annually by the Chemistry Club of the Georgia State College for Women "to the southern scientist selected for outstanding accomplishments in science." It was established in honor of Dr. Charles H. Herty, who was one of the speakers at the presentation.

THE Council of the Physical Society, London, has awarded the fifteenth Duddell Medal to Professor Hans Geiger, of the University of Tübingen. The medal is awarded to "persons who have contributed to the advancement of knowledge by the invention or design of scientific instruments, or by the discovery of materials used in their construction."

Industrial and Engineering Chemistry reports that in recognition of their public services the following chemists have been elected to the National Institute of Social Sciences: Jerome Alexander, Charles H. Herty, H. E. Howe, James L. Howe, D. D. Jackson and E. R. Weidlein.

THE University of Montreal has conferred the doctorate of science on Dr. M. L. Fernald, Fisher professor of natural history at Harvard University. The presentation was made preceding a course in botany given at the university by Dr. Fernald.

HAMLINE UNIVERSITY, St. Paul, Minn., will confer on June 6 the honorary degree of doctor of science on Dr. Mary B. Stark, professor and head of the department of histology and embryology at the New York Medical College and Flower Hospital.

DR. H. W. WADE, medical director of the Leonard Wood Memorial in the Philippine Islands, was the guest of honor on May 1 at a dinner given by the Medical Advisory Board of the memorial at the Union

League Club. The speakers included General Frank R. McCoy, Surgeon-General Thomas Parran, Dr. Wilbur A. Sawyer, Perry Burgess and Dr. Wade.

THE staff of Mount Sinai Hospital, New York City, gave a dinner on June 2 to Dr. Israel Strauss in celebration of his sixty-fifth birthday and "in honor of his many years of distinguished service in the hospital and the profession."

PROFESSOR EDWIN F. STIMPSON, member of the department of physics at the University of Kansas since 1901, is retiring at the end of this academic year on account of ill health.

DR. WILLIAM JEPSON, now in his fifty-second year of medical practice in Sioux City, Iowa, has been named professor emeritus of surgery in the Medical College of the University of Iowa. Dr. Jepson was head of the department of surgery from 1902 to 1912.

PROFESSOR JOHN C. GRAHAM, organizer and for twenty-seven years head of the department of poultry husbandry at the Massachusetts State College, will retire from active service on June 30.

DR. ARTHUR N. ALLING, since 1902 clinical professor of ophthalmology at the Yale School of Medicine, with which he has been associated for forty-five years, will retire this year. Dr. Alling has served as attending surgeon and ophthalmologist-in-chief at the New Haven Hospital and the New Haven Dispensary since 1914. As consultant in ophthalmology he will continue his connections with these institutions.

DR. HARRY MILES JOHNSON has been appointed professor and head of the department of psychology in the College of Arts and Sciences of Tulane University. He will succeed Dr. John M. Fletcher, who will retire at the close of the current session.

DEAN GEORGE D. STODDARD, of the Graduate College of the State University of Iowa, has been made head of the department of psychology. He also is director of the Iowa Child Welfare Research Station.

PROMOTIONS in the science departments at the University of New Hampshire have been announced as follows: Dr. Clark L. Stevens, professor of forestry, and Dr. George W. White, professor of geology. Dr. O. T. Zimmerman has been appointed associate professor of chemical engineering; Dr. Lloyd C. Fogg, associate professor of zoology; Dr. James A. Funkhouser and Dr. Charles M. Mason, associate professors of chemistry, and Dr. Edward B. Atkinson, assistant professor of chemistry.

PROFESSOR N. F. MOTT, of the University of Bristol, England, will teach a special course in the physics of metals in the summer session of the University of Pittsburgh from July 5 to August 12. Associated with him will be Dr. F. Seitz, of the General Electric Company; Dr. John Bardeen, of Harvard University; Dr. Francis Bitter, of the Massachusetts Institute of Technology, and Dr. Foster C. Nix, of the Bell Telephone Laboratories, New York.

DR. W. L. BRAGG, Cavendish professor of experimental physics in the University of Cambridge, has been elected professor of natural philosophy in the Royal Institution, London, in succession to the late Lord Rutherford. Professor Bragg is the son of Sir William Bragg, Fullerian professor of chemistry and director of the Royal Institution.

THE Board of Regents of the University of the State of New York has appointed Malcolm B. Galbreath, assistant in agricultural education at Cornell University, to be director of the New York State School of Agriculture at Morrisville, effective on July 1. Mr. Galbreath will succeed I. M. Charlton.

WALTER J. MOXOM, formerly first assistant, has been made chief of the St. Louis Office of the Weather Bureau. He succeeds Roscoe Nunn, who has been connected with the bureau for forty-seven years.

RONALD F. LEE, acting assistant director of the Branch of Historic Sites of the National Park Service, has been appointed chief of the branch.

DR. PIERRE LECOMTE DU NOÜY, director of advanced studies at the Sorbonne, Paris, formerly associate member of the Rockefeller Institute for Medical Research, arrived in New York City on May 24. He plans a study of the organization of scientific research in the United States.

DR. T. G. YUNCKER, professor of botany at DePauw University, assisted by some of his students, is spending the months of July and August making collections in the mountainous regions of northern Honduras.

GERALD FITZGERALD, of the U. S. Geological Survey, sailed from Seattle on May 14 to make aerial cartographic photographs of a tract in the Tanana Valley, Alaska, from Fairbanks to the international boundary. He was accompanied by J. M. Haynie, detailed from the Hydrographic Office of the Navy Department to assist in the Tanana project, and by J. Mark Holmes, detailed from the Topographic Branch to make topographic surveys of the western part of Chichagof Island and adjacent islands. Fred H. Moffit left Washington on May 18 to make geologic and mineral resources investigations in a portion of the Alaska Range at the head of Copper River, Alaska—an area that recently has been mapped topographically by the survey. T. W. Ranta left on May 20 to make topographic surveys near Nabesna in the Copper River region, Alaska.

OFFICIAL delegates from the United States to the second International Congress of Anthropological and Ethnological Sciences which opens on August 1 in Copenhagen are: Frans Blom, director of the Middle American Research Institute at Tulane University; Henry B. Collins, Jr., U. S. National Museum; Dr. Henry Field, Field Museum of Natural History; Dr. Aleš Hrdlička, U. S. National Museum, and Dr. Sylvanus G. Morley, Carnegie Institution of Washington.

DR. FRANCIS E. LLOYD, professor of botany, emeritus, McGill University, delivered on May 21 the annual Phi Beta Kappa–Sigma Xi lecture at the University of Oregon. His subject was "The Carnivorous Plants of the World."

THE eighth International Congress of Industrial Accidents and Occupational Diseases is to be held at Frankfort-on-Main from September 26 to 30. The president of the congress is Professor Martineck, of the Prussian Ministry of Labor. The secretary-general is M. Bauer, adviser of the same ministry. It is expected that a group of members of the Permanent Committee for America will attend the congress. Dr. R. R. Sayers, of the U. S. Public Health Service, is president of this group.

Nature states that the third International Congress of Tropical Medicine, which was to have been held at Amsterdam, and the third International Malaria Congress, which was to have been held at Madrid, had both been postponed, but that a joint congress will be held at Amsterdam from September 24 to October 1 under the presidency of Dr. G. Gryns. Further information can be obtained from the Secretary, Mauritskade 57, Amsterdam.

THE twenty-first annual meeting of the American Society of Ichthyologists and Herpetologists will be held from July 20 to 23. Sessions will be held on Wednesday and Thursday under the auspices of the Museum of Vertebrate Zoology, in the Life Sciences Building of the University of California. A trip to Stanford University is planned for Friday, and a visit to the Fleishhacker Zoological Garden and to the California Academy of Sciences, including the Steinhart Aquarium, will be made on Saturday. Titles and abstracts of papers to be presented should be sent to Dr. Jean M. Linsdale, Museum of Vertebrate Zoology, Berkeley, California, before June 20. The American Society of Mammalogists will meet in Berkeley at the same time.

WITH appropriate ceremonies planned and supervised by a committee of undergraduates, the cornerstone of the new physical science building at Kansas State College was laid on April 20. Speakers included Governor Walter A. Huxman, of Kansas; Dr. J. T. Willard, formerly head of the department of chemistry, now college historian; Dr. H. H. King, head of the department of chemistry, and Professor J. O. Hamilton, of the department of physics.

THE Marine Laboratory of the University of Maine at Lamoine will hold its sixth session under the direction of the department of zoology, from July 6 to August 12, offering a course in marine invertebrate zoology to graduate and undergraduate students. The facilities of the laboratory have been greatly improved during the past year. Dr. Edward G. Reinhard, professor of biology at the University of Scranton, and Dr. B. R. Speicher, assistant professor of zoology, University of Maine, will have charge of instruction. Six academic credits, graduate and undergraduate, are given for satisfactory completion of the course.

AT the fourteenth scientific sessions of the American Heart Association, to be held at the Sir Francis Drake Hotel, San Francisco, on June 10 and 11, Dr. William J. Kerr, of San Francisco, will deliver the presidential address on "Relief of Pain in Angina Pectoris." Dr. Carl J. Wiggers, of Western Reserve University, will give the annual address, his subject being, "The Dynamics of Hypertension," and Dr. Eliot R. Clark, of the University of Pennsylvania, will give the George Brown Memorial Lecture on "Certain Aspects of the Behavior of Peripheral Blood Vessels as Observed Microscopically in the Living Mammal."

THE Buffalo Museum of Science was this year's host to the New York State Geological Association at their fourteenth annual meeting on May 13 and 14. The program consisted of a field trip on May 13 to Eighteen Mile Creek to study the Devonian section and to observe the shores of glacial Lakes Warren and Whittlesey; the annual dinner at the Buffalo Trap and Field Club on Friday evening, and a field trip to the Niagara Gorge on Saturday, May 14, to study the Silurian stratigraphy and the Gorge's history. On Saturday evening the exhibits and work rooms of the museum were open for the inspection of the geologists. The program was in the charge of the president, Irving G. Reimann, curator of geology at the Buffalo Museum of Science. Speakers at the dinner were Chauncey J. Hamlin, president, the Buffalo Society of Natural Sciences; Professor George B. Cressey, chairman of the department of geology, Syracuse University; Dr. Harold L. Alling, professor of geology, the University of Rochester; Irving G. Reimann, association president, and Dr. Robert Wesley Brown, professor of geology, St. Lawrence University, president-elect. Dr. Richard F. Morgan, of the University of Buffalo, was toastmaster. It was voted to hold next year's meeting in the Adirondack area. Dr. Robert Wesley Brown was elected president, and Dr. J. S.

Brown, geologist of the St. Joseph Lead Company, Edwards, N. Y., was chosen as secretary. In addition to the members from New York State, there were delegates from Pennsylvania, New Jersey, Massachusetts, New Mexico and Ontario.

THE Massachusetts Institute of Technology has received a gift of $647,700 from Dr. Godfrey L. Cabot, of Boston. The income from the gift, which will be known as the Solar Energy Fund, will be devoted specifically to a search for direct methods of converting the sun's radiant energy into useful power or storing such energy for future use. These investigations will be continued for at least fifty years, after which the fund may be used for such other purposes as the corporation of the institute may select. To assist in the direction of these investigations, the following committee has been appointed: Professors Hoyt C. Hottel, department of chemical engineering; Arthur C. Hardy, department of physics; Ernest H. Huntress, department of chemistry; Arthur R. von Hippel, department of electrical engineering, and George W. Swett, department of mechanical engineering.

ON March 25 and 26 the new Building for Biological Sciences at the University of Oklahoma was dedicated. This building was made possible through a gift of $204,000 from the PWA authorities, and was equipped by a special appropriation of approximately $47,000 made by the Legislature of Oklahoma. Dr. Lorande Loss Woodruff, protozoologist of Yale University, was a special guest for the occasion, delivering two lectures, "Paramecium, Past and Present" and "Philosophers in Little Things." The building was officially dedicated by President William Bennett Bizzell, of the university, who spoke on "The University, Biology and the State." At the luncheon which was given for guests of the university, representing twenty-four institutions of higher learning, the following short addresses were given: "A Biologist Views Teachers and Teaching," by Dr. Roy W. Jones, of the Central State Teachers College at Edmond; "A Biologist's Land of Opportunity," by Dr. J. Clifford Shirley, of Phillips University, Enid, and "An Economic Entomologist Afield in Oklahoma," by Dr. F. A. Fenton, Oklahoma A. and M. College, Stillwater.

A SEPARATE department for the study of chemical engineering has been established by the trustees of Lafayette College and will probably open next September. The department will be centered in the mechanical engineering building. Alterations made there will provide for laboratory and classroom facilities. It is expected that apparatus will be constructed during the summer months, $4,000 having been granted by the trustees for this purpose.

DISCUSSION

SCIENCE AND GENERAL EDUCATION

IN establishing a Committee on the Improvement of Science in General Education, the American Association for the Advancement of Science has given substantial evidence of its interest in a problem of the most serious importance to the general public. A brief account of the organization of this committee has already appeared (SCIENCE, May 20), and a statement from the officers of the committee may be expected shortly; meanwhile some additional discussion seems justified by the hope that it may lead to more widespread interest. As one of the members of the committee, I am venturing some remarks.

The task which confronts this committee is that of doing what it can to improve the science instruction of the great mass of people who do not go into science as a profession. To accomplish anything towards this end will require cooperation on the part of the whole scientific fraternity and in particular the teachers of science.

It should be made clear at the outset that the committee has no warrant for thinking that it will discover any panacea. The problem is too complex and involved for that. There is, nevertheless, good reason to believe that much can be accomplished through arousing interest in the problem, providing a center for the collection and comparison of information and making known to teachers the results of such work. The experimental study on which this assumption rests will be referred to below.

There is increasing evidence that the problem of adequate science instruction for the bulk of our population is not confined to the upper levels of the educational system. Nevertheless, it seems most practical at this time for the committee to proceed with the problem as it exists in colleges and universities offering "Liberal Arts" courses in the sciences. The difficulty has been that, even in this type of course, the interests of future specialists usually dictate the selection of subject-matter and the mode of its presentation, even though there may be few if any such students present. This is in part simply a natural but regrettable consequence of the type of training which college and university teachers uniformly receive.

A number of attempts have been made to remedy this situation by providing an entirely different sort of course for the general student. These courses have frequently been launched under the lukewarm approval of the scientists themselves. We need very much to know whether the first scientific training of future specialists and non-specialists in the same

course is really impossible or at least undesirable. There is some evidence that it is neither, provided that the problem presented by the mixture of students is recognized and honestly faced.

Because the rank and file of the scientific profession consists of very busy and preoccupied individuals, it may be well to make clear the occasion for any study of science instruction in relation to general education. In general the colleges and universities of America are performing an excellent task in training professional scientists. On the other hand, there is abundant proof that the general public is not scientifically minded except in a very superficial sense. In particular it does not realize how science might contribute much more to social well-being than at present.

The scientist himself is well aware that society derives much less from the discoveries of science than it might. Though the more salable discoveries of science are usually taken up with remarkable speed, others that might be of even greater benefit to society are neglected because they are of a less commercial character. In private, at least, the scientist often expresses his disappointment that men in positions of authority do not adopt a more scientific and impersonal attitude in approaching social problems. Often, too, he is distressed to know that his budgets are the first to suffer when expenses have to be cut.

While science has produced revolutionary changes in our manner of daily living it has scarcely touched many aspects of our behavior and attitudes of mind which were developed under far different conditions from those which science has made possible. The persistence of these older forms of thought and behavior into the modern world to which they have little relationship is a source of increasing maladjustment. People are not as able as they should be to adapt themselves to the conditions of modern living and to contribute to the intelligent direction of public affairs. As is always the case when a culture is not well harmonized throughout, there are tragic and unnecessary conflicts within society and within the individual.

Increasing numbers of thoughtful people are becoming concerned over this unhappy lack of harmony in our culture, at the same time being aware that this culture is depending increasingly upon science. Some seriously believe that harmony can be achieved only by slowing down the activity of the sciences. Others believe that the remedy will come only through the unremitting prosecution of scientific research and its application in technology.

Either of these view-points represents an extreme. The basis of the problem is neither a matter of less nor more rapid scientific development, but a better integration of scientific attitude with individual and social behavior. The scientist himself represents a very small minority of society. In consequence, the problem is largely one of educating the general public. It is to the study of this problem that the new committee has addressed itself. As has been said, it can hope to make little progress without the activity of its professional colleagues. Whether these view the problem from the narrow angle of enlightened self-interest or the broader basis of citizenship in a troubled modern world, it is hoped that their generous aid will be forthcoming. Without anticipating the specific questions which the committee will propound in its forthcoming statement, it may be pointed out here that recent studies give a basis for hoping that good may be accomplished. Reliable techniques have been developed for estimating the extent to which the aims of any educational program are achieved. In a recent study, for example, it was found that

(a) Many teachers have given so little thought to formulating their conscious aims that they find at first considerable difficulty in doing so.

(b) There is a great diversity of aims as stated by those who teach general courses in the same subject.

(c) Once the aims of any particular course are stated clearly it is quite possible to measure the degree to which they are being achieved.

(d) Such inquiry results in measurable improvement in the general teaching of a science.

There is thus reason to hope that similar inquiry extended over a broader field might make it possible to discover some measure of common aim and to suggest means by which these aims would be better achieved in the interest of general education than at present.

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GRANTS IN SUPPORT OF RESEARCH ON THE BIOLOGICAL EFFECTS OF RADIATION

IN this journal indications have been furnished, from time to time,[1] regarding grants in support of research on the effects of radiation on organisms. During a period of somewhat more than eight years the Committee on Radiation of the Division of Biology and Agriculture, National Research Council, has been able to make these grants as a result of contributions made specifically for this purpose. In continuation of the program of the last three-year period, 1935–38, on the Biological Effects of Radiation, the committee announces a limited program for 1938–39 (July 1, 1938, to June 30, 1939) made possible through a new contribution of $25,000 from the Rockefeller Foundation.

[1] W. C. Curtis, SCIENCE, 69: 9–10, January 4, 1929; SCIENCE, 73: 643–645, June 12, 1931; B. M. Duggar, SCIENCE, 82: 125, August 9, 1935.

The purpose of these grants is to encourage and assist in maintaining researches directed primarily to the solution of fundamental biological problems, and to the development of apparatus essential in such studies. In making short-term grants, as for 1938–39, special consideration will be given to work in progress or to programs definitely formulated. Next in importance to the scientific promise of the project is the availability of facilities and of cooperation in case the work involves other fields, such as special chemical or physical techniques. The committee endeavors to keep in touch with interested industrial corporations manufacturing apparatus or materials used in such biological studies, and in the past the cooperation of these agencies has been valuable both for the loan of certain types of apparatus and for assistance in the construction of special facilities.

Applications for grants should be made promptly, and these should include an adequate statement of the status of the problem or project, the extent of the support received or promised, or the time offered, by the university or institution with which the applicant is associated and the character of the apparatus available or obtainable for the work.

The conditions under which grants of money or apparatus may be made are essentially the same as those made by the Committee on Grants-in-Aid of the National Research Council, and in brief are as follows:

1. Grants will cover such expenses as apparatus, materials and supplies, technical assistance, and, to a limited extent, field expenses.

2. Ordinarily, grants will not be made for any part of the personal salary of the grantee, for expenses of publication, for the purchase of books or for travel in attendance upon scientific meetings.

3. In general, preference will be given to the support of investigations, (a) requiring a moderate allotment, (b) from which definite results may be expected with the aid of the grant, (c) which are supported in part by the institution with which the applicant is associated, and (d) for which it is reasonably certain that the facilities are available or procurable, or in which cooperation is arranged between the biological and physical interests.

It is expected that allotments for 1938–39 will be made in late August. Those planning to apply for grants should immediately request application forms from the Division of Biology and Agriculture, National Research Council, 2101 Constitution Ave., Washington, D. C. The applications, together with any supporting documents, should be sent promptly, preferably by July 15, 1938, to the Division of Biology and Agriculture.

B. M. DUGGAR,
Chairman, Committee on Radiation

NEWTON'S THIRD LAW

THE recent discussions of "Osgood's Mechanics," by J. W. Campbell and H. M. Dadourian (SCIENCE, November 12, 1937, and April 29, 1938) prompts me to add a comment. In my experience students usually fail to distinguish between the equality of opposite forces in equilibrium and the equality of forces expressed by Newton's third law. It is therefore disconcerting to find this confusion on page 1 of Osgood's excellent text. He says: "Thus if a barrel of flour is suspended by a rope (and is at rest), the attraction of gravity—the pull of the earth—will be represented by a vector pointing downward and of length W, the weight of the barrel. On the other hand, the force which the rope exerts on the barrel will be represented by an equal and opposite vector, pointing upward. For, action and reaction are equal and opposite."

But the weight of the barrel and the force which the rope exerts on the barrel are not related as action and reaction. The reaction to the weight is not the force exerted by the rope, but the pull of the barrel on the earth. Forces in equilibrium act on the same body, whereas action and reaction act on different bodies. A principle of equilibrium is therefore not derivable from the third law. I remark that "An Advanced Course in General College Physics" by Bayley and Bidwell contains a precise statement of the distinction.

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SOCIETIES AND MEETINGS

SOUTHWESTERN DIVISION OF THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

THE Southwestern Division of the American Association for the Advancement of Science held its eighteenth annual meeting at Albuquerque, New Mexico, from April 25 to 28, 1938. The University of New Mexico was host institution.

The meetings were very well attended in all sections. The following organizations met in conjunction with the division: The Mathematical Association of America, Southwestern Section; Society of American Foresters, Southwestern Section; American Association of University Professors, Rocky Mountain Region; and New Mexico Section, American Society of Civil Engineers.

The following officers were elected for the coming year: *President,* E. F. Carpenter, University of Arizona, Tucson; *Vice-president,* J. R. Eyer, New Mexico State College, Las Cruces; *Secretary-Treasurer,* Veon C. Kiech, University of New Mexico, Albuquerque. *Executive Committee*—S. A. Northrop, University of New Mexico; D. S. Robbins, Las Cruces, New Mexico; F. W. Sparks, Texas Technological College, Lubbock; Emil Haury, University of Arizona, Tucson; F. E. E. Germann, University of Colorado, Boulder.

Officers of the various sections for the coming year were announced as follows:

Biological Science: Chairman, W. H. Bell, University of New Mexico, Albuquerque; *Secretary,* C. K. Cooperrider, U. S. Forest Service, Tucson.

Mathematics Section (Southwest Section Mathematical Association of America): Chairman, R. S. Underwood, Texas Technological College, Lubbock; *Secretary,* Harold D. Larsen, University of New Mexico, Albuquerque.

Physical Science Section: Chairman, E. J. Workman, University of New Mexico, Albuquerque; *Secretary,* C. W. Botkin, New Mexico State College, Las Cruces.

Social Science Section: Chairman, V. J. Smith, Sul Ross Teachers College, Alpine, Texas; *Secretary,* J. Charles Kelley, Sul Ross Teachers College, Alpine, Texas.

Future meeting places of the division were scheduled as follows: Alpine, Texas, with Sul Ross Teachers College and the McDonald Observatory as host institutions for 1939; Tucson, Arizona, with the University of Arizona in 1940; Lubbock, Texas, with Texas Technological College in 1941.

Of the resolutions passed unanimously the following is of general interest:

Since first they were founded nearly a thousand years ago, Universities have always been homes for research—homes for the discovery and dissemination of truth. They have been and should still be both the preservers of the best that civilization has attained and extenders of the bounds of knowledge in every field of human interest. This work has been accomplished because universities have been free to seek for and to proclaim the truth when discovered. To-day we note with the deepest regret, which should be showed by all people, that universities in many parts of the world are no longer free. Some have been reduced to agencies for propaganda for special ideas and isms with no scientific foundation. Not all of our own universities are entirely free from the same sort of pressure from special groups, but happily they have not been prostituted in the same way as has happened abroad.

We therefore wish to emphasize in the strongest possible terms our belief that any such interference with the unrestricted freedom of universities to search for and to proclaim the truth according as the evidence points is fatal to sound and continued progress. We would further urge all who love truth and freedom to protect against any such interference, if and when it is attempted, with all the power at their command.

With the cooperation of the Soil Conservation Service, a general symposium was held on the topic, "The Results of Soil Conservation." Papers were presented on the topics: "Soil Conservation Service Activities in the Southwest," by Herbert C. Stewart, head of the section of erosion control practices, Soil Conservation Service, and "Research of the Soil Conservation Service in the Southwest," by Thomas Maddock, associate engineer, Soil Conservation Service.

A symposium of special interest was held in the Physical Science Section on "Meteorology," headed by R. H. Byers, head of the Air Mass Analysis Section, U. S. Weather Bureau, Washington, D. C., with other papers by E. F. George, department of physics, Texas Technological College, and by R. E. Holzer and E. J. Workman, both of the department of physics of the University of New Mexico.

Another symposium of particular interest was held in the Biological Science Section on "Syphilis," papers being presented by Myrtle Greenfield, New Mexico State Public Health Laboratory; Willis Barnes, University of New Mexico; Julian O. Long, health officer for District No. 3, Santa Fe, New Mexico; and E. F. McIntyre, New Mexico Bureau of Public Health.

The Section of Mathematics featured a symposium on the "Teaching Problems in Mathematics," and addresses by E. R. Hedrick, provost, University of California, Los Angeles, and Aubrey J. Kempner, University of Colorado.

The John Wesley Powell Lecture, an annual address for the general public, was presented by E. R. Hedrick, on the topic of "Relations of Science to Economics and to War."

The retiring president's address, delivered by F. E. E. Germann, was on the topic, "The Occurrence of Carbon Dioxide, with Notes on the Origin and Relative Importance of Subterranean Carbon Dioxide," at an evening banquet session.

The Rocky Mountain Region of the American Association of University Professors heard addresses on the topics of "Place and Function of Faculties in University Government," by E. R. Hedrick; and "University Administration in the Americas," by Dean Harold Benjamin, University of Colorado.

Social events included an informal tea to all visitors at the home of Dr. J. F. Zimmerman, president of the university, and various affairs for the visiting ladies by wives of the faculty members of the University of New Mexico.

The sessions were closed by an all-day excursion, the

route of which covered 170 miles and included inspection of methods of control in the U. S. National Forests, with forestry officials acting as guides; visits to modern Indian Pueblos and sites of ancient pueblos where archeological work is being done. The route of the excursion led the party through a portion of the state which is of very great geologic as well as scenic interest.

VEON C. KIECH,
Secretary

SPECIAL ARTICLES

BROMINATION OF OPTICALLY ACTIVE METHYLPHENYL- AND PROPYL-PHENYL-CARBINOLS

IT is the general conclusion of physical chemists that every reaction of substitution by a negative group or atom following a bimolecular course is connected with a Walden inversion. Granting that in the majority of reactions thus far observed this conclusion is valid, yet there is evidence that the conclusion is not *generally* valid. In the higher members of the homologous series of methylphenylcarbinols, from propylphenylcarbinol on, the reaction of bromination by means of hydrogen bromide gas proceeds, predominantly, without inversion. Certain considerations led us to investigate the effect of the temperature on bromination from 160° C. to − 80° C. Dry hydrogen bromide gas was allowed to act on the carbinol. At 0° C. the reaction was practically instantaneous. The rotation of the bromide formed from *propylphenylcarbinol* (carbinol and bromide rotating in the same direction) increased markedly with lowering of the temperature of reaction.

At the higher temperatures of reaction, the rotation of the bromide formed from *methylphenylcarbinol* under similar conditions is opposite to that of the carbinol. The bromide showed a small increase in rotation with a drop in temperature, but *when the reaction proceeded at about − 35° C. and at all lower temperatures, the rotation of the bromide obtained changed sign, the reaction then proceeding without inversion.*

The results are summarized in Table 1.

Thus it is evident that at every temperature two simultaneous reactions take place—one with, the other without inversion. At lower temperatures the latter predominates. That is, the reaction proceeds without inversion when the hydroxyl group has a higher mobility than the other three groups, for then the asymmetry of the molecule remains unchanged during the reaction of substitution. The reverse takes place at higher temperatures. The reason perhaps is that the mobility of the hydroxyl group has a lower temperature coefficient than that of the other groups.

TABLE 1

Methylphenylcarbinol $[M]^{25}_{5780.1} = -41.5°$

Propylphenylcarbinol $[M]^{25}_{5780.1} = -49.1°$

Compounds	Methylphenylbromomethane				Propylphenylbromomethane			
Temperature of Bromination	0 °C	− 30 °C	− 35 °C	− 80 °C	160 °C	0 °C	− 50 °C	− 65 °C
$[M]^{25}_{5780.1}$	+ 13.5°	+ 36.4°	−22.6°	− 27.0°	− 1.3°	− 41.7°	− 146.5°	− 154°

This observation may also have a practical significance, since by the changes in rotation with the lowering of temperature of the reaction, it may be possible to discern whether a reaction of substitution took place with or without inversion.

A complete report will be published elsewhere.

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IS AGGLUTINATION AN EXPLANATION FOR THE OCCURRENCE AND FOR THE CHROMOMERE-TO-CHROMOMERE SPECIFICITY OF SYNAPSIS?

No current hypothesis accounts adequately for the occurrence of synapsis between homologous chromosomes. Still less do these hypotheses, electrical or otherwise, account for the one-to-one specificity displayed by hundreds of different pairs of chromomeres at synapsis.

The hypothesis here considered is that synapsis of homologous chromosomes is a process comparable to agglutination of a given kind of bacteria or blood corpuscles.

A necessary preliminary to the agglutination of a given bacterium is the formation of its specific antibody or antibodies. For example, when a rabbit is injected with bacteria, the surface materials of the

bacteria (antigens) stimulate the formation of antibodies by the animal and these accumulate in its blood. When such immune serum is mixed with a suspension of the exciting bacterium, the bacteria adsorb the corresponding antibodies upon their surfaces (antigen-antibody union) and become capable of adhering specifically to each other. Previous to the mixing of the antibody and the bacteria, the bacteria remained separate, apparently repelled by similar electrical charges. Removal of the mutual repulsion, by neutralization of the individual electrical charges, is apparently a general non-specific step in the agglutination mechanism. There seem to be no "attractive" forces involved, but contacts are brought about through random movements due to currents, to temperature agitation or to motility of the organism itself. When two bacteria coated with the same antibody chance to meet, a union is formed through the antibodies, and agglutination or clumping follows.

An animal may simultaneously produce antibodies against an indefinitely large number of kinds of bacteria. Also, immunization against one bacterium often results in the production of five or more demonstrably different antibodies and probably others which have not been demonstrated. All these antibodies act together simultaneously without interference in affording the animal protection against a simultaneous multiple infection.

Topley, Wilson and Duncan[1] showed that when a heterogeneous mixture of bacteria is agglutinated by a heterogeneous mixture of the specific antisera, each cluster of bacteria is homogeneous. The "forces" which determine the formation of clusters containing each a particular kind of bacterium are specific so that each cluster is a lattice of identical unions through the adsorbed antibodies.

The present hypothesis proposes that the specificity of chromomere synapsis is similarly effected by one or more specific agglutinins for each of the different chromomeres. The surface of each chromomere may be assumed to stimulate in the protoplasm the formation of specific antibodies just as do the surface antigens of each type of bacteria. It is not necessary that the contained genes themselves act as antigens (although they may do so), since the nucleoproteins of the envelope overlying each chromomere would be sufficient. The molecules of antibody which then chance to come in contact with the corresponding chromomere surface are adsorbed. Each chromomere thus becomes specifically capable of adhering to its partner chromomere and couples with it upon contact.

After the leptotene threads are produced in sperm- or egg-mother-cells, any two allelic chromomeres which touched would be cemented together by the antibody junctions specific for themselves. The chromomeres which are on each side of the already agglutinated ones would then be more likely to touch and fuse, so that synapsis would proceed, zipper-like, from the first points of homologous contact throughout the entire lengths of the chromosomes.

Since all the chromomeres of a given kind are coated with the same antibody, synapsis in auto-triploids or tetraploids could include all strands. Such inclusive synapsis for triploids and tetraploids is observed to be the case in the salivary gland pseudo-synapsis, and was formerly believed to be the general case. However, if meiotic synapsis occurs predominantly or exclusively in pairs (Darlington), then this would be similar to the formation of separate clumps in agglutination. In triploids, strands *a* and *b* would usually come into contact at different points than strands *b* and *c*, and pairing would proceed from the separate contact points.

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[1] W. W. C. Topley, J. Wilson and J. T. Duncan, *Brit. Jour. Exp. Path.*, 16: 116, 1935.

ROOT AND SHOOT PRODUCTION INDUCED IN CABBAGE BY BETA (3) INDOLE-ACETIC ACID

At the suggestion of Professor George K. K. Link a study of the responses of cabbage to applications of Beta (3) indole-acetic acid was undertaken. Paste containing 30 mg of the acid per gram of lanolin was applied to decapitated first internodes of young seedlings. This treatment resulted not only in the production of an apical ring of adventitious roots, as reported for other plants, among them bean and tomato, but also in the production of viable shoots.

The first cellular response of cabbage upon application of the paste was enlargement of the cells underlying the cut, shortly followed by rapid cell divisions in the rays, phloem, parenchyma and endodermis. Root primordia were organized from the proliferated cells of rays and phloem, and their apical histogens were apparent by the end of 144 hours. Mounds of external callus tissue were produced on the cut surface, mostly over the phloem, and within them matured irregular areas of vascular tissue intermingled with highly meristematic regions in a very confused pattern.

Many of the decapitated and treated plants then developed shoots, which were detectable in 288 hours after treatment. They were found to arise either in the external callus or from internal callus (in the sense of Jost and Link) considerably below the cut surface at the level of adventive root production. Origin of shoots from internal callus was less fre-

quent than from the external callus. Most shoots arose from external callus produced by the pith and by the phloem, though in some cases the xylem and endodermis also were involved to a small extent. These regenerated shoots always established organic union with the vascular tissue of the decapitated shoot and became functional.

This observation of shoot regeneration by cabbage following treatment with Beta (3) indole-acetic acid is not an instance of induction of a new characteristic by a chemical agent. Occasionally (very rarely) decapitated control cabbage plants produced shoots without application of the acid. The chemical treatment apparently merely induces the internal conditions requisite for expression of a capacity which normally rarely comes to expression in the cabbage plant.

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EXACT PROBABILITIES IN CARD-MATCHING PROBLEMS

A DECK of mn playing-cards composed of m suits of n cards each, may be arranged in $(mn)!/(n!)^m$ ways. If one of these is compared with some standard order, the number of coincidences is called the score. The frequency of any score r may be denoted by (r ; m,n). Huntington[1] gave the values of (r ; 3,3) and (r ; 4,4). He considered the labor in the determination of (r ; 5,5) to be prohibitive. Sterne[2] found the values of (21 ; 5,5) up to (25 ; 5,5) but knew of no way to determine these for smaller r. Greville[3] has recently found all values of (r ; 5,5); his solutions are correct, but involve much labor.

The problem is by no means as difficult as these papers imply. Macmahon[4] gave a direct method of attack by which Greville's results may be checked with about 12 hours of machine calculation. I have recently determined the values of (r ; m,n) for all m and n less than 7 (m and n not being necessarily equal). The frequencies for the case in which both m and n are 6 are given in Table 1.

TABLE 1

6 × 6

Score	Frequency								
0 ...		4	165	949	769	769	961	828	425
1 ...		28	996	446	742	915	700	420	640
2 ...		98	700	744	213	619	952	591	700
3 ...		218	864	808	829	456	293	367	200
4 ...		355	341	281	078	962	422	086	175
5 ...		450	116	994	274	568	927	912	160
6 ...		462	909	014	435	100	202	332	336
7 ...		397	123	967	735	823	016	052	640
8 ...		289	793	784	100	001	073	868	710
9 ...		182	524	670	735	530	786	230	560
10 ...		100	344	596	349	272	804	505	000
11 ...		48	575	943	371	163	005	793	504
12 ...		20	851	099	196	639	140	076	850
13 ...		7	980	545	109	018	220	394	400
14 ...		2	735	656	277	729	448	992	400
15 ...			842	844	533	954	374	188	000
16 ...			234	038	576	801	926	712	520
17 ...			58	693	462	370	532	698	400
18 ...			13	313	942	477	144	955	600
19 ...			2	734	372	820	642	421	600
20 ...				508	679	897	516	240	400
21 ...				85	715	584	272	352	800
22 ...				13	076	448	757	088	400
23 ...				1	804	316	455	605	600
24 ...					224	849	404	787	850
25 ...					25	255	852	293	600
26 ...					2	550	498	318	360
27 ...						230	827	143	200
28 ...						18	656	661	150
29 ...						1	339	048	800
30 ...							85	377	840
31 ...							4	709	664
32 ...								243	135
33 ...								8	640
34 ...									540
35 ...									0
36 ...									1
	2	670	177	736	637	149	247	308	800

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1 Huntington, SCIENCE, 86: 499–500.
2 Sterne, SCIENCE, 86: 500–501.
3 Greville, *Journal of Parapsychology*, March, 1938.
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